

SPACE ENVIRONMENTAL EFFECTS ON LDEF LOW EARTH ORBIT EXPOSED GRAPHITE
REINFORCED POLYMER MATRIX COMPOSITES

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INTRODUCTION

The Long Duration Exposure Facility (LDEF) was deployed on April 7, 1984 in low earth orbit (LEO) at an altitude of 482 kilometers. On board experiments experienced the harsh LEO environment including atomic oxygen (AO), ultraviolet radiation (UV), and thermal cycling. During the 5.8 year mission the LDEF orbit decayed to 340 kilometers where significantly higher AO concentrations exist. LDEF was retrieved on January 12, 1990 from this orbit.

One experiment on board LDEF was M0003, "Space Effects on Spacecraft Materials". As a subset of M0003 nearly 500 samples of polymer, metal and glass matrix composites were flown as the "Advanced Composites Experiment" M0003-10. The Advanced Composites Experiment is a joint effort between government and industry with the Aerospace Corporation serving as the experiment integrator. A portion of the graphite reinforced polymer matrix composites were furnished by the Boeing Defense & Space Group, Seattle, Washington.

This paper presents test results and discussions for the Boeing portion of M0003-10. Experiment and specimen location on the LDEF are presented along with a quantitative summary of the pertinent exposure conditions. Matrix materials selected for the test were epoxy, polysulfone and polyimide. These composite materials were selected due to their suitability for high performance structural capability in space craft applications. Graphite reinforced polymer matrix composites offer high strength to weight ratios along with excellent dimensional stability.

The Boeing space exposed and corresponding ground control composite specimens have been subjected to post flight mechanical, chemical, and physical testing in order to determine any changes in critical properties and performance characteristics. Among the more significant findings are the erosive effect of atomic oxygen on leading edge exposed specimens and microcracking in non-unidirectionally reinforced flight specimens .

The M0003-10 Advanced Composites Experiment was located at both the leading and trailing edges of the LDEF as shown in Figure 1. The leading edge specimens were at position D8 on the satellite which was 38 degrees from the direction of motion (ram direction). The trailing edge specimens were located at position D4, 158 degrees from the ram direction.

The specimens of experiment M0003-10 were intentionally positioned at both leading and trailing edges in order to provide varied exposure conditions. At the mission altitudes the atomic oxygen was swept by the LDEF leading edge surface. The trailing edge specimens received practically no atomic oxygen exposure.

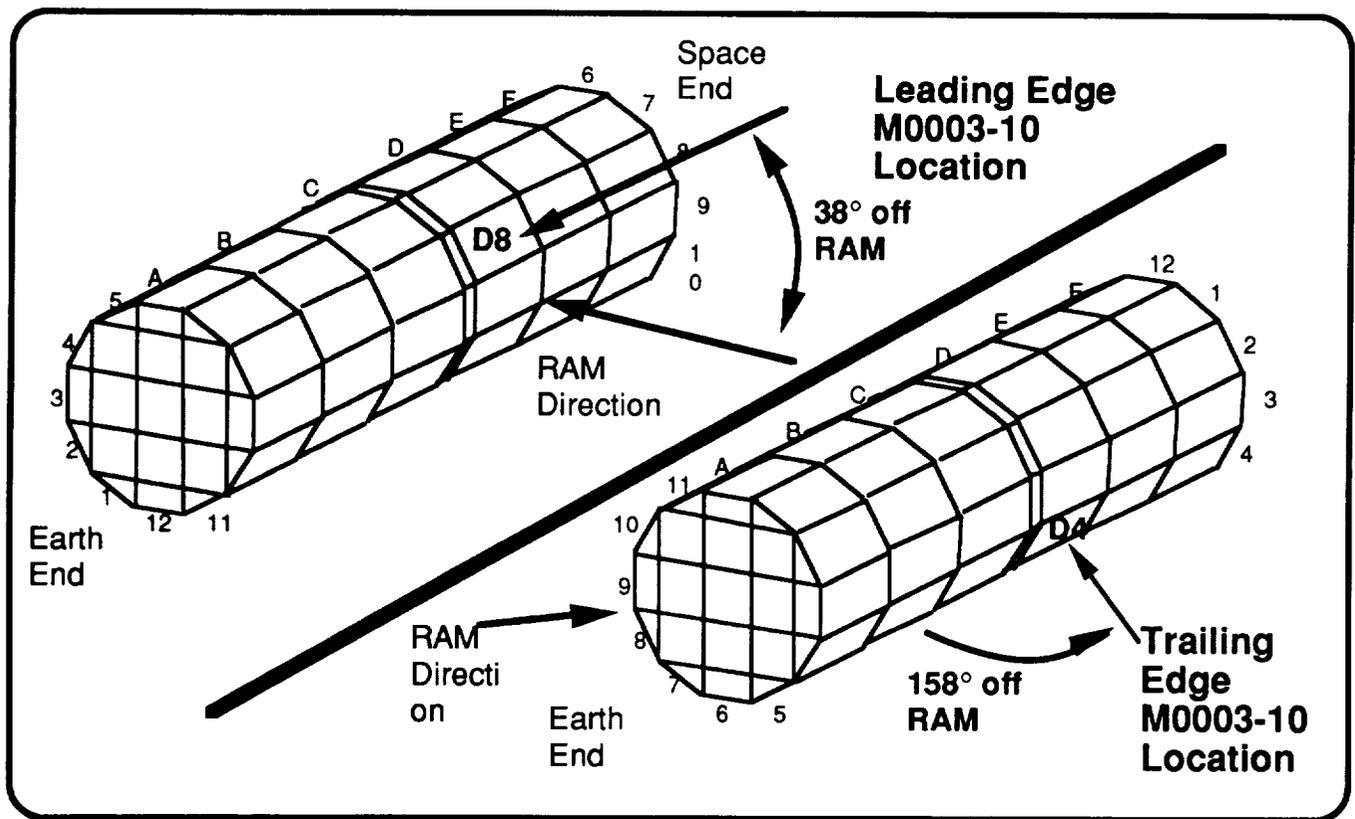


Figure 1. Location of M0003-8 experiment on LDEF

Graphite fiber reinforced polymer matrix composites were located at both the leading and trailing edge positions as shown in Figure 2. Complete sets of the five material types listed in Figure 2 were flown in both direct space exposure positions on the "A-deck" as well as in shielded positions on the "B-deck" at the leading and trailing edges. Also, a complete set of specimens were kept at controlled temperature and humidity conditions at the Aerospace Corporation. These specimens were shielded from exposure to ambient light and were used as ground controls.

Specimen configuration was 3.5 inches long by 0.5 inches wide with the 0 degree direction parallel to the length. Thickness of the specimens varied between matrix types due to differences in number of plies and ply thickness. Matrix resins and reinforcements along with ply stacking sequences for the specimens are listed in Figure 2. The original documentation does not list the specific type of reinforcement for the LARC 160 polyimide. However it is known that the fibers are of the low modulus (33 Msi) range as are all of the reinforcing fibers for these specimens.

The epoxy specimens represented the state of the art for epoxy systems at the time of experiment integration. The polysulfone specimens were selected due to their excellent outgassing properties as well as their potential for on orbit manufacture and repair. The polyimides represent the upper end of temperature capability for polymer matrix composites

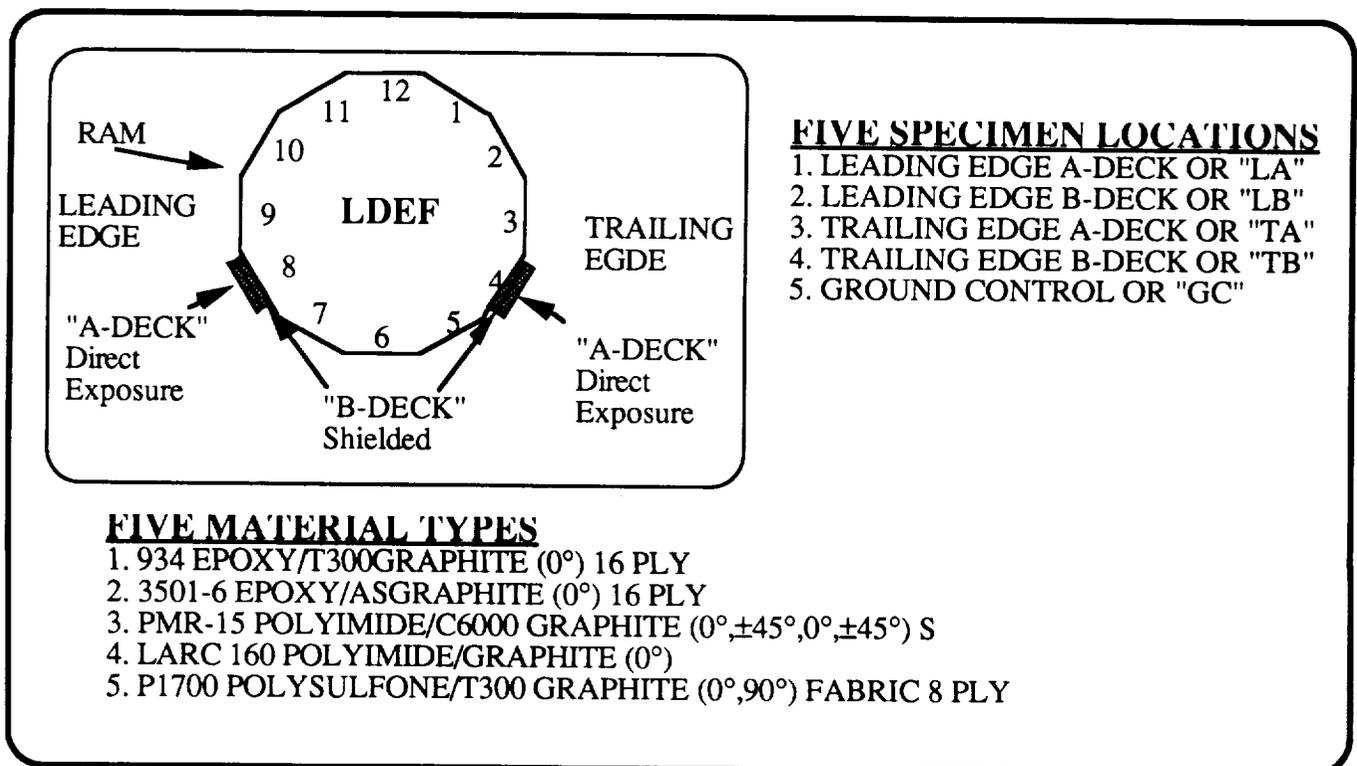


Figure 2. Material types and locations

Table 1 lists the exposure conditions for the flight test specimens at the leading and trailing edge A-deck positions as well as for the shielded B-deck positions. The leading edge A-deck specimens were exposed to relatively high fluxes of atmospheric constituents, primarily highly reactive atomic oxygen at the altitudes involved with the LDEF mission. Solar, including ultraviolet, and particulate radiation were similar for leading and trailing edge A-deck specimens. B-deck specimens did not receive any AO or UV exposure.

Thermistor data collected by the Aerospace Corporation from leading and trailing edge instrumented A-deck specimens indicates significant thermal cycling of the composites during the flight.¹ B-deck thermistor data was not available. However, the thermal coupling of the specimens was designed such that temperature excursions for the A and B deck were to be similar. Microcrack data presented later in this paper suggests that the B-deck specimens may have experienced milder temperature excursions and/or milder thermal shock conditions.

Table 1. ATOMIC OXYGEN, SOLAR EXPOSURE AND THERMAL CYCLING

	LEADING EDGE "A-DECK" ,ROW 8	TRAILING EDGE "A-DECK" ,ROW 4	LEADING & TRAILING EDGE "B"DECK
ATOMIC OXYGEN EXPOSURE (Impacts / cm ²)	6.93 x 10 ²¹	9.32 x10 ⁴	0
INCIDENT SOLAR & EARTH REFLECTED RADIATION (Equivalent solar hours)	9,300	10,500	0
THERMAL CYCLING (In Flight Measurement)	-53°F to 183°F 32,422 CYCLES	-27°F to 170°F 32,422 CYCLES	Unknown, B-deck expected to be less than Adeck, leading expected to be less than trailing

Two to four specimens of each material were flown at each position (and ground control). One each was dedicated to chemical and physical testing. The remaining specimens were tested for mechanical properties. The tests performed are listed in Figure 3 along with the potential uses of the resulting data.

The specimens were configured as 3.5 inch by 0.5 inch strips for flexure testing. Although flexure testing is not the preferred method of the designer, it allows good relative performance measurements. The data collected is useful for determining mechanical performance degradations between exposure and ground control specimens.

Chemical testing by infrared (IR) spectroscopy can reveal the changes in organic functional group chemistry. Energy dispersive X-ray spectroscopy (EDX) is a sensitive technique for measuring the elemental composition of surfaces. These test results may help to determine the underlying degradation mechanism of atomic oxygen on polymer matrix composites.

Physical tests include glass transition temperatures as measured by thermomechanical analysis (TMA), surface recession by mass loss and microcracking by cross sectional microscopy, total mass loss (TML) and volatile condensable materials (VCM) by outgassing tests, and coefficients of thermal expansion by dilatometry. These test results are valuable for determining dimensional stability and outgassing characteristics.

MECHANICAL: FLEXURE MODULUS AND STRENGTH

- ROUGH DESIGN KNOCKDOWN ESTIMATES FOR UNCOATED COMPOSITES IN LEO APPLICATIONS
- VERIFICATION OF LEO SIMULATION AND MODELING
- RESISTANCE TO LEO EFFECTS OF COMPOSITES WITH DAMAGED PROTECTIVE COATINGS

CHEMICAL: IR SPECTROSCOPY AND EDX

- UNDERLYING MECHANISM FOR DEGRADATION OF PERFORMANCE PROPERTIES DUE TO LEO EXPOSURE

PHYSICAL: GLASS TRANSITION, SURFACE RECESSION, MICROCRACKING, TML & VCM, AND CTE

- KNOCKDOWN IN USE TEMPERATURE CAPABILITY DUE TO RESIN DEGRADATION
- STRUCTURAL PERFORMANCE REDUCTION DUE TO LEO EXPOSURE
- RESIDUAL OUTGASSING PROPERTIES
- THERMAL EXPANSION PROPERTIES

FIGURE 3. PROPERTIES MEASURED - POTENTIAL USES OF DATA

Figures 4 through 8 show the flexure test results for the space exposed, shielded and ground control specimens. Three point flexure testing was performed per ASTM D790 using an Instron model TT-D equipped with a deflectometer. A cross head speed of 0.1"/minute and a 21T span to depth ratio were used. All testing was performed at room temperature.

The 934 epoxy/T300 graphite specimens did not show any significant loss in flexure properties between the different positions on LDEF and the ground control. These results are based on the post flight cross-sectional areas. The loss of material for the leading edge exposed specimens results in a performance reduction for a given specimen. As these specimens were unidirectionally (0°) reinforced, the load that would have been carried by the eroded material on the leading edge exposed specimens was carried by the remaining 0° material. For these specimens the only mechanical performance loss was due to material loss on the leading edge exposed specimens. Ply orientation plays a significant role in flexure properties behavior when AO erosion is involved.

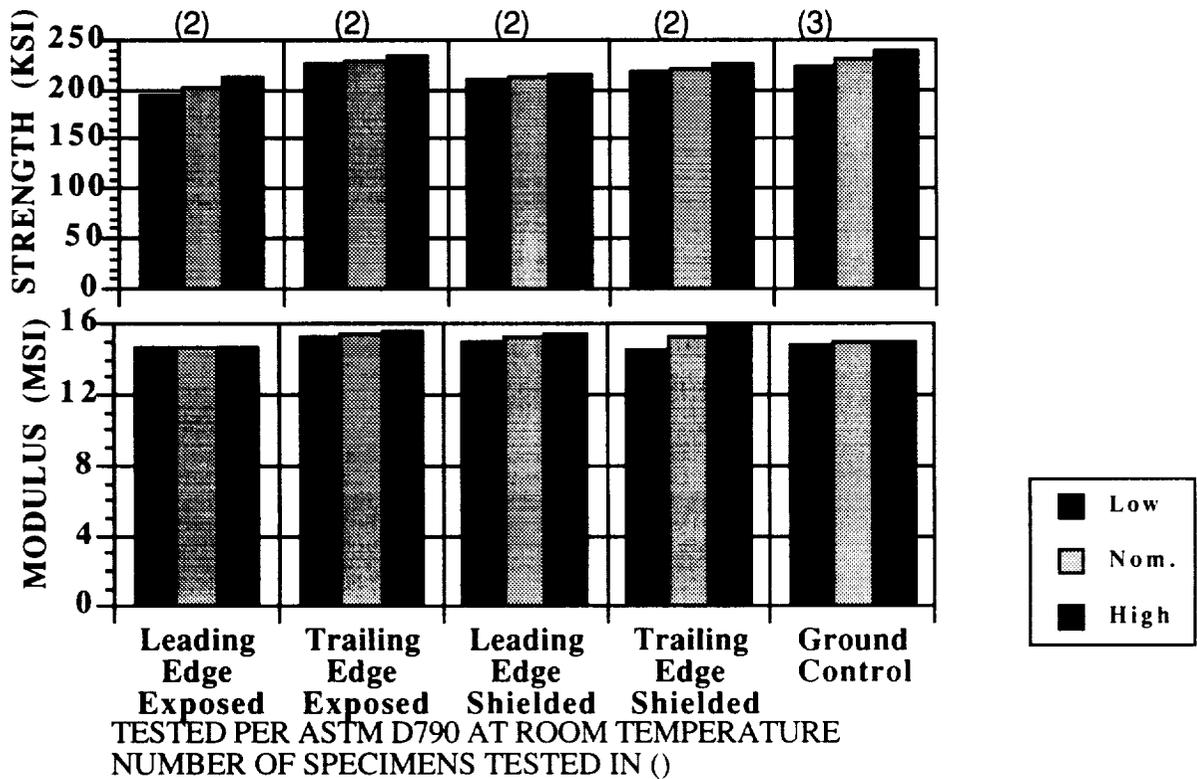


Figure 4. Flexure strength and modulus of 934/T300 specimens, (0°) 16 plies

The 3501-6 epoxy/AS graphite flexure test results show very little change in modulus values among the different exposure conditions and the ground control. The strength values show some variation from position to position, most likely due to the inherent scatter with polymer matrix composite strength measurements and the small sample size. Once again the 0° orientation of the reinforcement allows the underlying plies to pick up the load from the eroded surface ply on the leading edge exposed specimens. This is a similar situation to the 934/T300 results where mechanical performance reductions are due to erosion of material on the leading edge specimens.

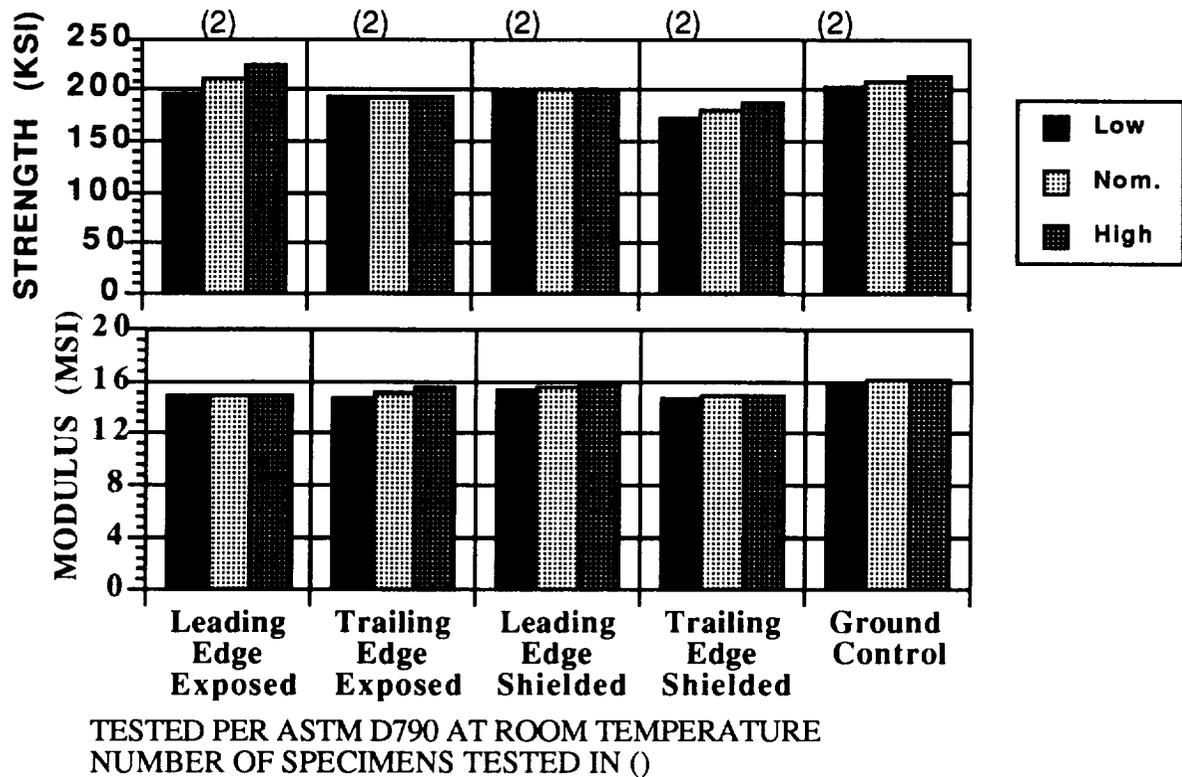


Figure 5. Strength and modulus of 3501-6/AS specimens, (0°) 16 plies

The P1700 polysulfone/T300 graphite specimens were reinforced with a 0°,90° woven fabric. Here also as with the unidirectionally reinforced specimens there is continuous reinforcement in the load direction in each ply. No significant changes in either flexure modulus or strength were found.

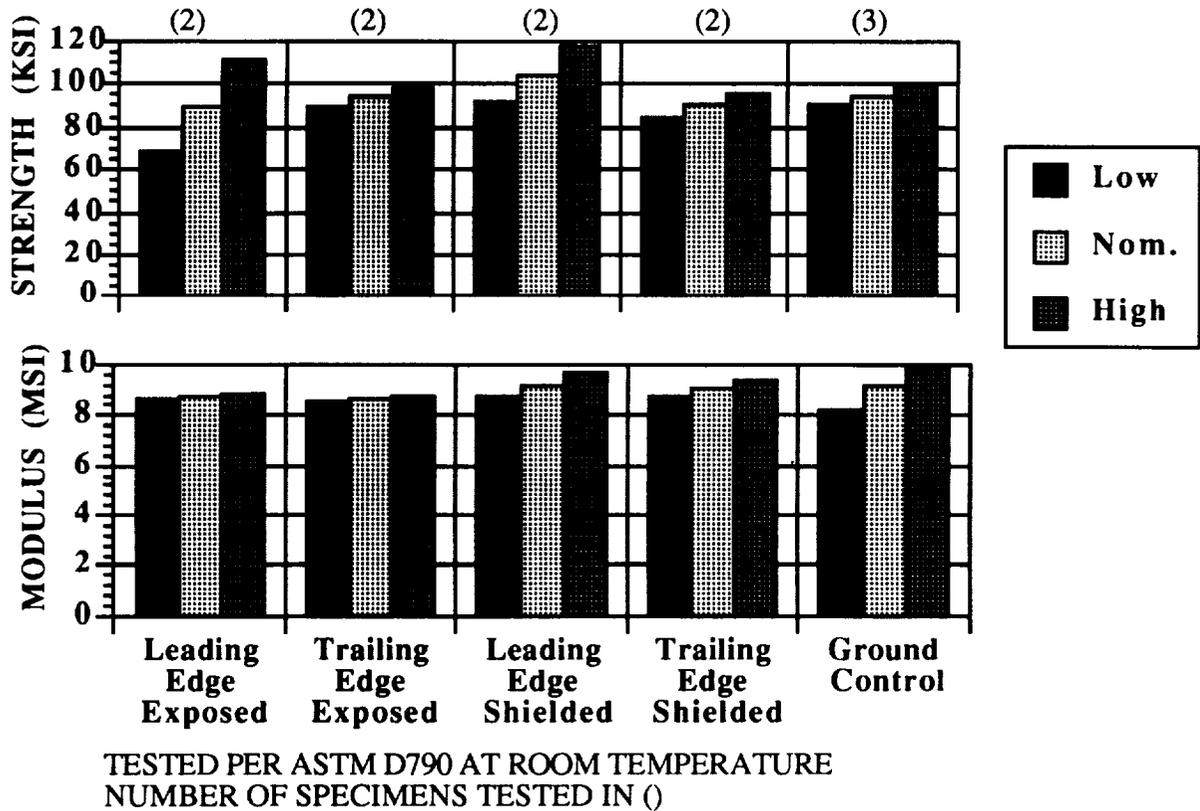


Figure 6. Flexure strength and modulus for P1700/T300 specimens, (0°,90°) fabric 8 plies.

The PMR-15 polyimide/ C6000 graphite specimens were reinforced with an angle ply stacking sequence of $(0^\circ, \pm 45^\circ, 0^\circ, \pm 45^\circ)_s$. As can be seen from the data in Figure 7 the strength and modulus values drop off significantly for the leading edge exposed specimens. This is due to the almost complete loss of the 0° ply on the exposed surface of the specimen due to AO erosion. Unlike the unidirectionally reinforced specimens, the ply underneath is at $+45^\circ$ and has a lower stiffness and strength in the load direction. This behavior has been seen in other leading edge LDEF specimens with multidirectional reinforcement.²

The non AO exposed specimen data show no significant change in flexure properties compared with the ground control data.

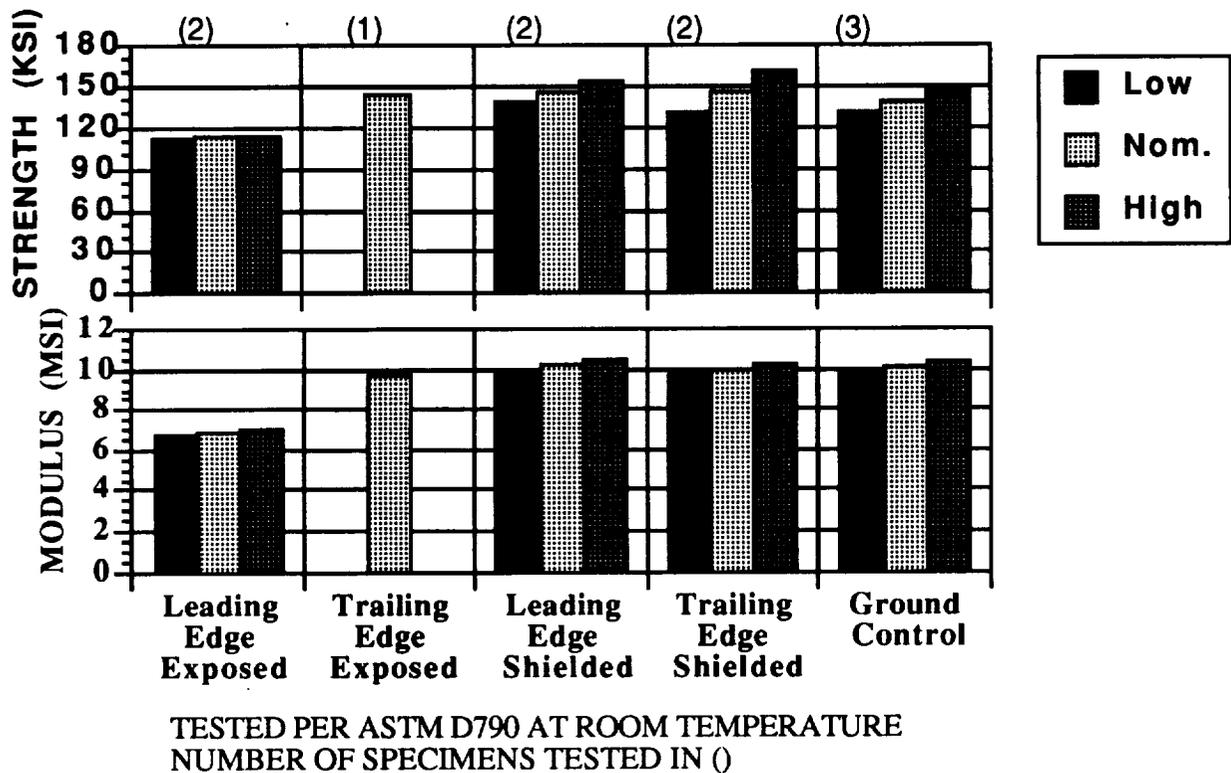


Figure 7. Flexure strength and modulus for PMR-15/C6000 specimens $(0^\circ, \pm 45^\circ, 0^\circ, \pm 45^\circ)_s$

The LARC 160 polyimide/ graphite flexure test results show very little change in modulus values among the different exposure conditions and the ground control. The strength values show some variation from position to position, most likely due to the inherent scatter with PMC strength measurements and the small sample size. Once again the 0° orientation of the reinforcement allows the underlying plies to pick up the load from the eroded surface ply on the leading edge exposed specimens. This is a similar situation to the other unidirectionally reinforced material results where mechanical performance reductions are due to erosion of material on the leading edge specimens.

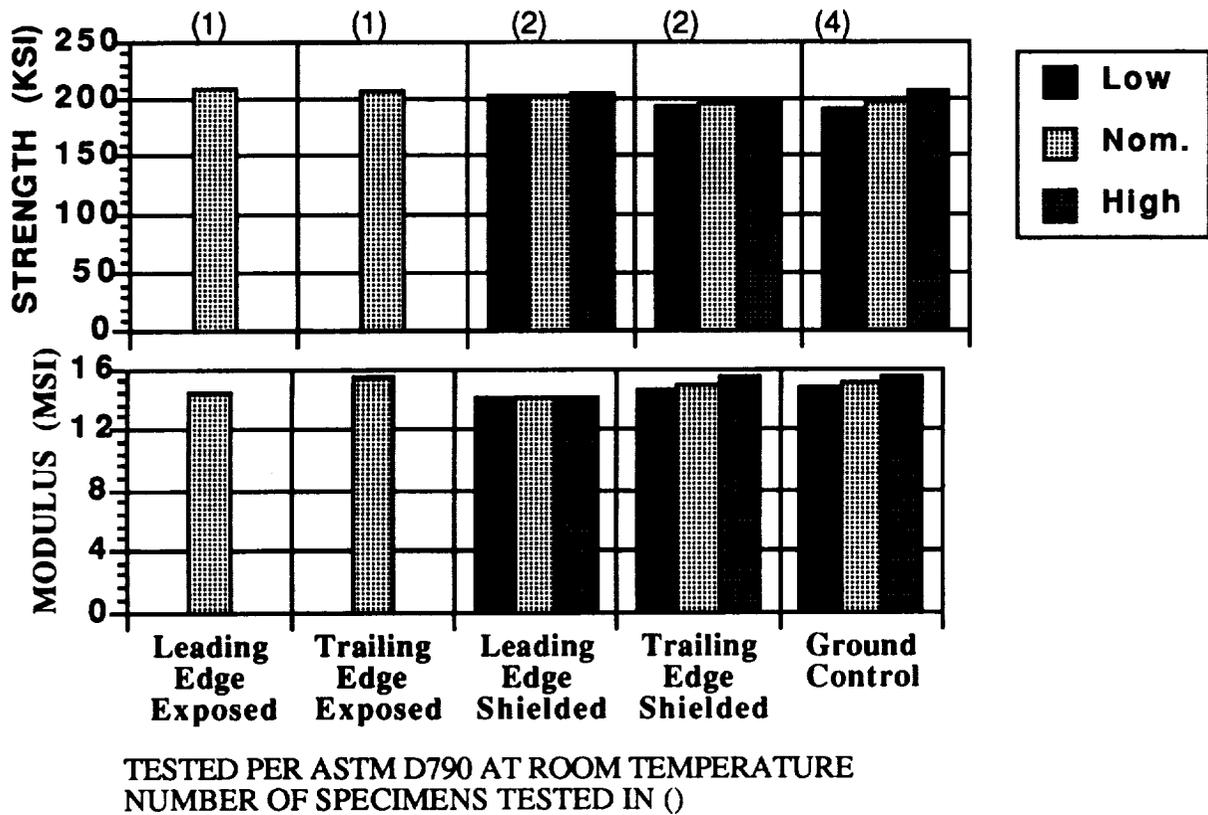


Figure 8. Flexure strength and modulus for LARC 160/graphite specimens, (0°)

Total mass loss (TML) and volatile condensable materials (VCM) measurements were made using the NASA-SP-R-0022A outgassing test. The test samples were held at 125°C and the collection plate at 25°C for 24 hours at 10⁻⁶ torr. The trailing edge 934/T300 specimens were not tested as this material was used for other purposes. The test results are presented in Table 2.

The exposed and shielded values compare favorably with the ground control values. After 5.8 years of space exposure including vacuum and temperature extremes one would expect these specimens to have thoroughly outgassed. Therefore the outgassing measured here is most likely due to moisture reabsorbed by the specimens during the 18 months between retrieval and testing. This phenomenon has been observed in dimensional change measurements performed on LDEF specimens by Tennyson.³

The TML outgassing levels for P1700 polysulfone/T300 graphite were an order of magnitude less than the other materials. This can be expected due to the thermoplastic nature and low polarity of the matrix resin.

TABLE 2. VOLATILE CONDENSABLE MATERIALS AND TOTAL MASS LOSS TEST RESULTS

LOCATION	934/T300 EPOXY		3501-6/AS EPOXY		PMR15/C6000 POLYIMIDE		LARC160/Gr. POLYIMIDE		P1700/T-300 POLYSULFONE	
	TML	VCM	TML	VCM	TML	VCM	TML	VCM	TML	VCM
LEADING EDGE EXPOSED	0.52	0.02	0.57	0.01	0.56	0.01	0.51	0.01	0.05	0.01
TRAILING EDGE EXPOSED	N.T.	N.T.	0.43	0.03	0.56	0.00	N.T.	N.T.	0.03	0.00
LEADING EDGE SHIELDED	0.43	0.00	0.41	0.02	0.57	0.02	0.71	0.01	0.08	0.00
TRAILING EDGE SHIELDED	N.T.	N.T.	0.43	0.01	0.59	0.00	0.63	0.02	0.04	0.01
GROUND CONTROL	0.39	0.01	0.56	0.02	0.53	0.02	0.68	0.01	0.06	0.01

NASA SP-R-0022A OUTGASSING TEST, 24 HOUR EXPOSURE

Thermomechanical analysis (TMA) in flexure was performed on specimen samples from each position including the ground controls. The trailing edge 934/T300 specimens were not tested as this material was used for other purposes. Testing was performed using a Perkin Elmer System 7 thermomechanical analysis unit using a 10° C /minute temperature ramp. The test results are presented in Table 3.

The exposed and shielded values compare favorably with the ground control values and with each other. This indicates that no significant thermal degradation of bulk polymer properties has occurred. No clear trends are perceivable concerning specimen position or material type. The value for the ground control P1700 polysulfone/T300 graphite sample is in doubt as the TMA trace curve began falling off in slope at the initiation of the temperature ramp indicating a sample mounting or measuring anomaly.

TABLE 3. GLASS TRANSITION TEMPERATURES

LOCATION	934/T300 EPOXY	3501-6/AS EPOXY	PMR15/C6000 POLYIMIDE	LARC160/Gr. POLYIMIDE	P1700/T-300 POLYSULFONE
LEADING EDGE EXPOSED	189°C	211°C	340°C	354°C	190°C
TRAILING EDGE EXPOSED	N.T.	216°C	336°C	340°C	180°C
LEADING EDGE SHIELDED	193°C	213°C	331°C	361°C	190°C
TRAILING EDGE SHIELDED	N.T.	214°C	336°C	354°C	180°C
GROUND CONTROL	191°C	211°C	335°C	352°C	167°C*

* This data point suspect due to possible mounting or measuring anomaly

Thermal expansion coefficients were measured in the 0° direction for each material using a Netzsch model 402 dilatometer. The dimensional change vs. temperature plots for the PMR-15 polyimide/C6000 graphite specimens shown in Figure 9 are representative of all the composite specimens. This plot includes values for leading and trailing edge shielded and exposed specimens as well as the ground control. The accuracy of this measurement technique is approximately 0.001% relative expansion as plotted. Therefore these measurements indicate no significant change in thermal expansion properties. However, as will be discussed in the following section, significant variations in microcracking in the PMR-15 polyimide / C6000 graphite specimens were found. This technique for measuring thermal expansion properties is not sensitive enough to measure the impact of this microcracking.

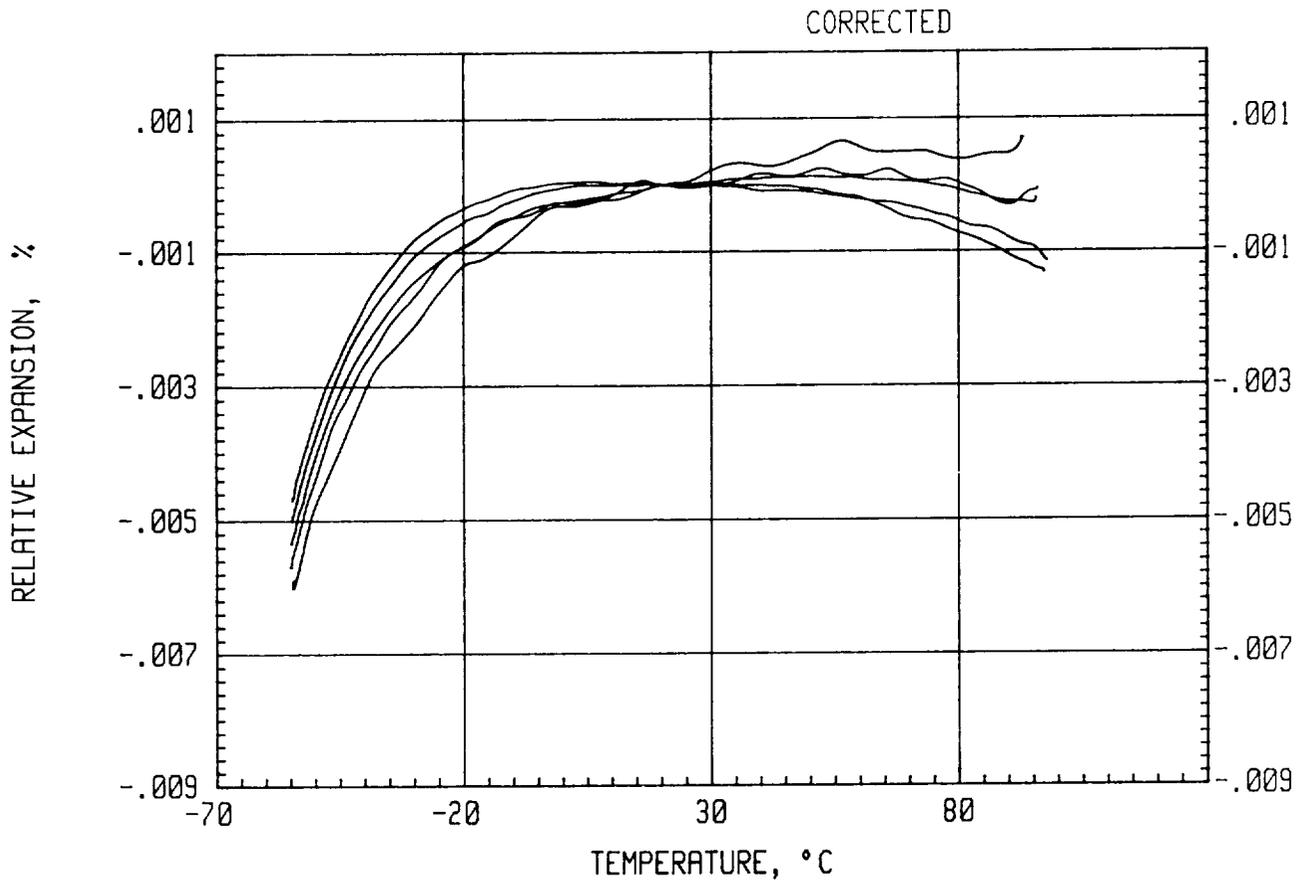


Figure 9.- Thermal expansion properties of PMR 15 polyimide/C6000 graphite LDEF specimens

Quantitative microcracking analysis was performed using optical microscopy on polished cross sections. These cross sections were taken perpendicular to the 0 degree direction and were examined at 100x magnification with the aid of a dye penetrant to enhance the contrast of the cracks. A total of 0.55 inches of lineal cross section was examined and the count of cracks was normalized to cracks per inch. Most of the surface ply of the leading edge exposed PMR-15 polyimide/C6000 graphite specimen was eroded away. The number of cracks per inch for the PMR-15 specimen was extrapolated to an estimated value as given in parenthesis in Table 4. Enough material remained for the leading edge exposed polysulfone specimen to obtain a crack count for the surface ply.

Most of the microcracks observed were intraply (within an individual ply). However some cracks in the PMR-15 polyimide/C6000 graphite did extend through two plies. Microcracking was only detected in the laminates with a nonunidirectional layup orientation. These laminates were the PMR-15 polyimide/C6000 graphite and the P1700 polysulfone/T300 graphite specimens which had $(0^\circ, \pm 45^\circ, 0^\circ, \pm 45^\circ)_S$ and $(0^\circ, 90^\circ)$ layup orientations respectively. The exposed (A-deck) PMR-15 and polysulfone PMC laminates specimens displayed the most microcracking. A smaller but significant level of cracking was found for the leading edge shielded (B-deck) PMR-15 and polysulfone PMC specimens. The trailing edge shielded (B-deck) PMR-15 and polysulfone PMC specimens displayed little or no microcracking. Ground controls did not display any microcracking.

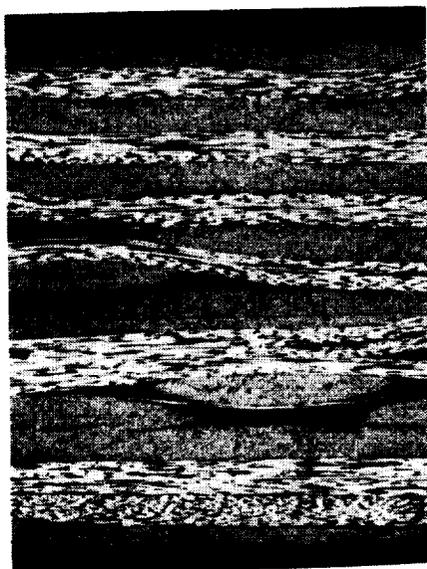
The non unidirectional layup produces greater thermally induced stresses as the part experiences thermal cycling. Also, the leading edge exposed specimens have a significantly higher emissivity due to the rough texture produced by atomic oxygen erosion.³ This may account for the colder extremes reported for the leading edge exposed specimens.² The shielded specimens may have experienced milder thermal cycling extremes as their microcrack densities were significantly lower than the exposed specimens.

TABLE 4. MICROCRACKING (MICROCRACKS/INCH)

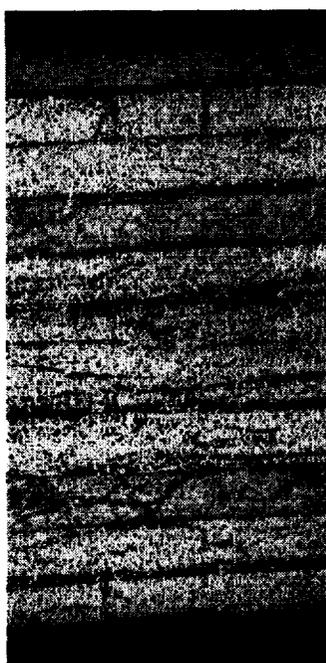
LOCATION	LDEF THERMAL CYCLING	934/T300 EPOXY (0°)	3501-6/AS EPOXY (0°)	PMR15/C6000 POLYIMIDE (0°, ±45°, 0°, ±45°) _S	LARC160/Gr. POLYIMIDE (0°)	P1700/T-300 POLYSULFONE (0°, 90°)
LEADING EDGE EXPOSED	-53°F to 183°F	0	0	33(45*)	0	35
TRAILING EDGE EXPOSED	-27°F to 170°F	0	0	47	0	35
LEADING EDGE SHIELDED	Less Than Above?	0	0	7	0	6
TRAILING EDGE SHIELDED	Less Than Above?	0	0	0	0	2
GROUND CONTROL	None	0	0	0	0	0

* extrapolation to account for eroded ply

Figure 10 shows a magnified cross sectional view of the leading edge P-1700 polysulfone/T300 graphite and PMR 15 polyimide/C6000 graphite specimens. These photomicrographs were taken at 50X and 100X magnification respectively. Intralaminar cracking can be seen in the outer plies of both specimens.



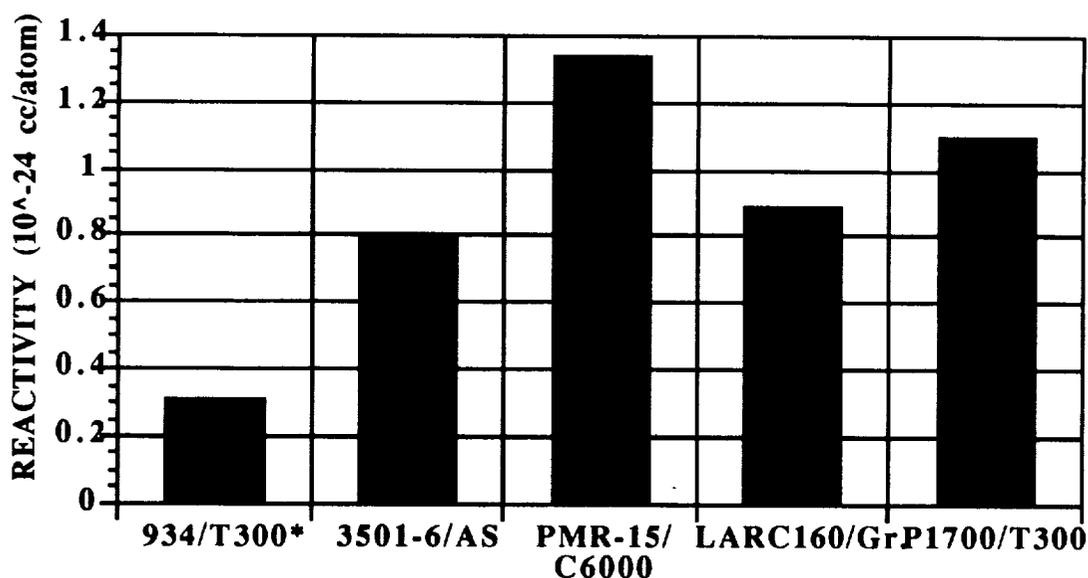
P-1700 polysulfone/T300



PMR 15 polyimide/C6000

Figure 10. Cross sectional micrograph of graphite reinforced polysulfone and polyimide specimens from the exposed leading edge position

Atomic oxygen reactivity values shown in Figure 11 for the five composite systems flown were calculated based on mass loss data. These values do not correspond well to the relative levels of local material loss as observed using optical microscopy. This suggests that other factors are involved in the mass loss of the whole specimen. Local areas of surface contamination were observed using scanning electron microscopy on many of the specimens. These areas appear to have experienced reduced or no erosion due to shielding by the contaminants. Other areas were observed with reduced erosion and no surface contaminant suggesting that a contaminant may have provided temporary shielding from atomic oxygen attack. Reactivity values for composite systems and any other material may best be obtained through local thickness loss measurements near a shielded area by microscopy or profilometry.



Calculated from weight loss data measured at the Aerospace corporation

* This value not consistent with cross sectional analysis

Figure 11. Atomic oxygen reactivity for leading edge exposed specimens

Figures 12 through 16 are scanning electron photomicrographs of leading edge specimens. Metallic coating of the specimens was not necessary as the conductivity of the graphite reinforcement was found to be sufficient. Perspectives and magnifications for each figure are similar allowing qualitative comparison of features.

Figure 12 shows the surface of a 934 epoxy/T300 graphite specimen. A jagged peak like structure exists with a stringy, "ash" like material concentrated in clumps around the peaks. The jagged peaks and "ash" structures are ubiquitous among the graphite reinforced specimens. However the level and texture of these features differ from composite type to composite type.



Figure 12. Scanning electron photomicrograph of leading edge exposed 934 epoxy/T300 graphite surface

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Figure 13 shows the surface of a 3501-6/AS graphite specimen. This material is very similar in chemistry to the 934 epoxy system. The jagged peak like structure and stringy, "ash" like material are present here in about the same level.

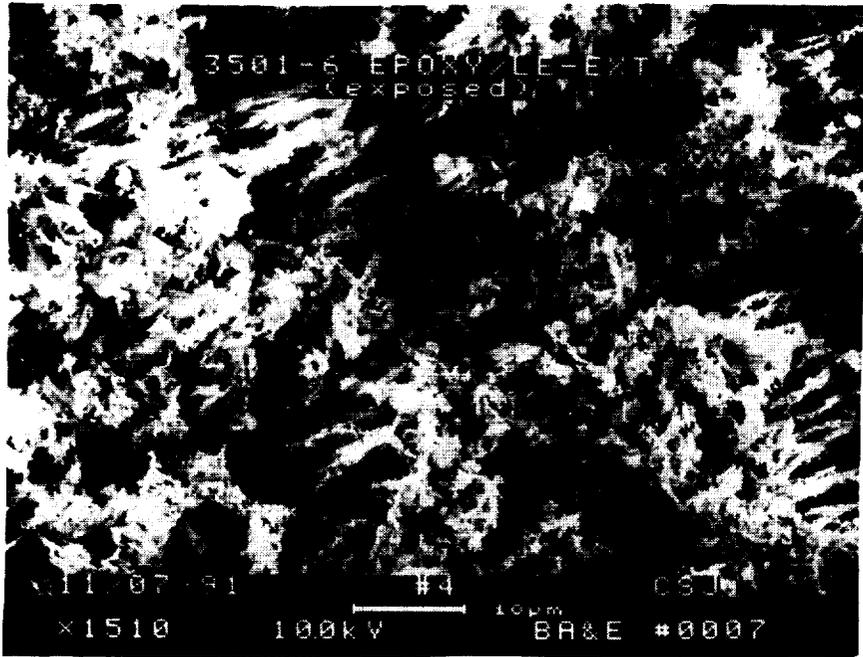


Figure 13. Scanning electron photomicrograph of leading edge exposed 3501-6/AS graphite surface

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Figure 14 shows the surface of a leading edge exposed P1700 polysulfone/ T300 graphite specimen. The size and texture of the jagged peaks and "ash" structure are more similar to the epoxies than the polyimides. The "ash" level appears to be less than with the epoxies and greater than the polyimides. Also visible in the photomicrograph are lines along the walls of the jagged peaks. It is not known whether these lines correspond to the fiber direction.

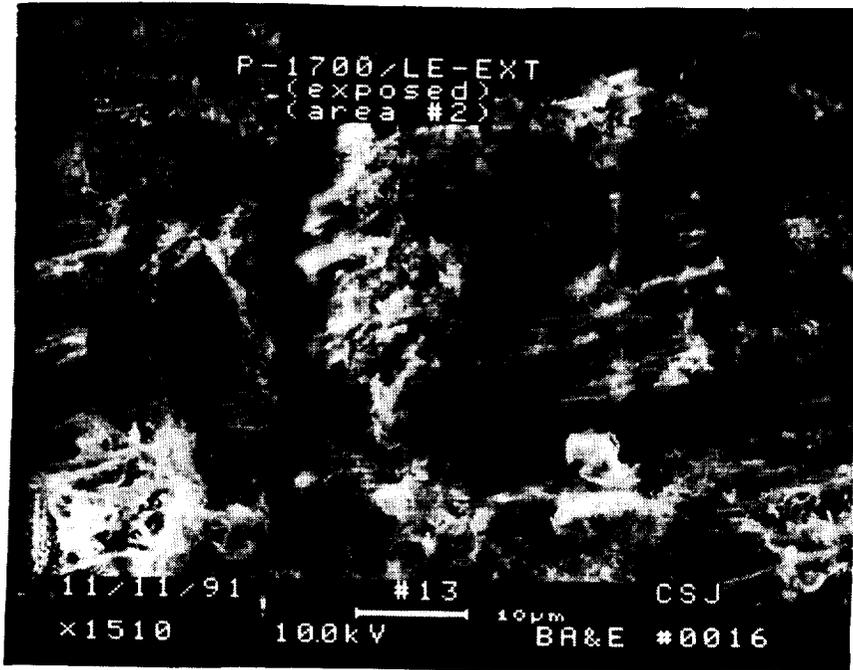


Figure 14. Scanning electron photomicrograph of leading edge exposed P1700 polysulfone/ T300 graphite surface

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The "ash" level for the PMR-15 polyimide/C6000 graphite shown in Figure 15 appears to be significantly lower than that of the epoxies. This "ash" is of a much finer texture resembling "cobwebs". Previous SEM work with LDEF specimens using metallic coatings to reduce charging did not reveal this structure for the PMR-15 polyimide.² The "ash" structure for the 934 epoxy specimens employing a metallic coating was visible and intact. This indicates that the "ash" structure for the PMR-15 polyimide is extremely delicate. The size and spacing of the jagged peaks for the PMR-15 polyimide appear larger than that of the epoxies.

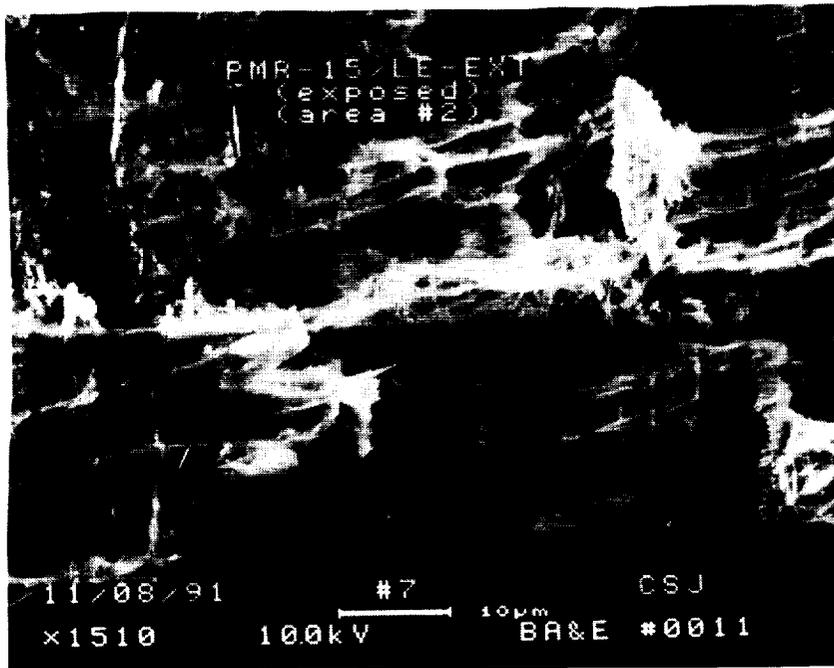


Figure 15. Scanning electron photomicrograph of leading edge exposed PMR-15 polyimide/C6000 graphite surface

Figure 16 shows the surface of a leading edge exposed LARC 160 polyimide/graphite specimen. The jagged peak size and spacing appear similar to the PMR-15 polyimide. The "ash" structure also appears similar with more "clumps" present. An area of contamination can be seen just to the left of the center. These areas were common on all leading edge exposed surfaces.



Figure 16. Scanning electron photomicrograph of leading edge exposed LARC 160 polyimide/graphite surface

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Figure 17 shows post flight infrared spectroscopy (IR) traces for material taken from two areas on the leading edge exposed surface of the 934 epoxy/T300 graphite specimen. An IR trace for the ground control specimen is also included. A Bio Rad Digilab FTS-60 fourier transform IR spectrometer equipped with a UMA 300A IR microscope was used to make all IR measurements.

Some obviously significant changes have occurred to the surface of these specimens during LEO exposure. The two leading edge exposed surface traces indicate that little if any of the original matrix material is present on the surface. Both traces are dominated by broad single peaks with various shoulders. The "long flaking coating" trace peak matches that of a silicate indicating that this material may be a contaminant. The "long flaking" appearance is consistent with that of other ubiquitous LDEF silicate contaminants.

The peak for the "particles on surface" trace is clearly shifted to the right compared to the silicate peak. This material is the "ash" seen on the surface of the exposed 934 epoxy specimen SEM photomicrographs.

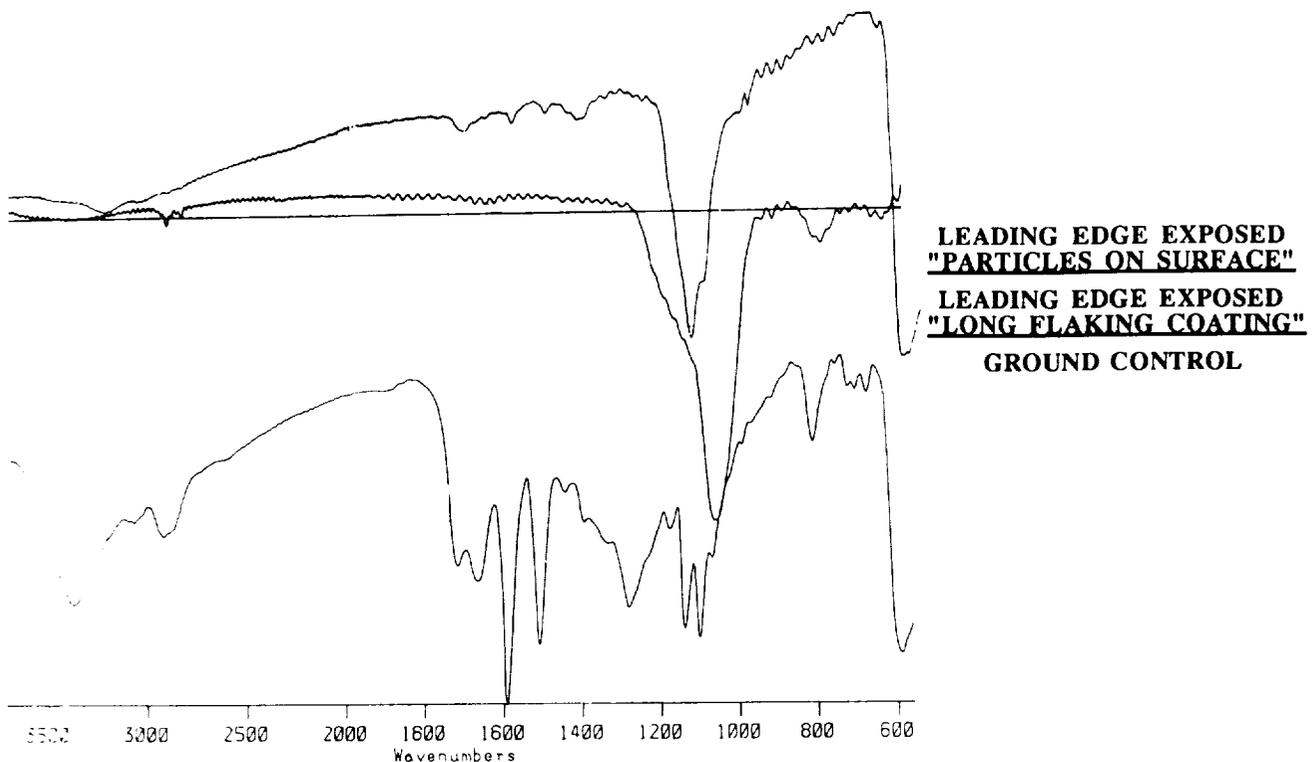


Figure 17. FTIR spectroscopy trace for 934 epoxy/T300 graphite specimens

The IR spectroscopy traces for the 3501-6 epoxy/AS graphite in Figure 18 resemble those of the 934 epoxy. The peak on the "surface scrape" trace occurring in the 1100-1200 wavenumber region matches that of the peak from the 934 epoxy "particles" trace. These peaks match the IR spectra of sodium sulfate very well as reported in earlier efforts.² The presence of a peak in this area has also been reported for 5208 epoxy/T300 graphite leading edge exposed specimens.⁴ The presence of sodium and sulfur on the 934 epoxy surface has been detected by EDX and is reported later in this paper. Also, X-ray diffraction techniques have confirmed the presence of orthorhombic crystalline sodium sulfate with a high degree of confidence for both the 934 epoxy and P1700 polysulfone composites. This suggests that sodium sulfate is present in the ash of both the 934 epoxy and P1700 polysulfone leading edge exposed specimens.

The presence of sodium sulfate on only certain polymer matrix composites suggests that contamination from other LDEF sources is improbable. One possible source of this compound is that residual sodium contamination from manufacture of graphite fiber tows is combining with sulfur from the composite matrix material curing agent to form AO resistant sodium sulfate. This may offer an explanation for the light and dark banded pattern reported for a 5208 epoxy/T300 graphite specimen flown on LDEF.⁵ The banding may be due to variations in the residual levels of sodium in or on the carbon fiber tows from the manufacturing process.

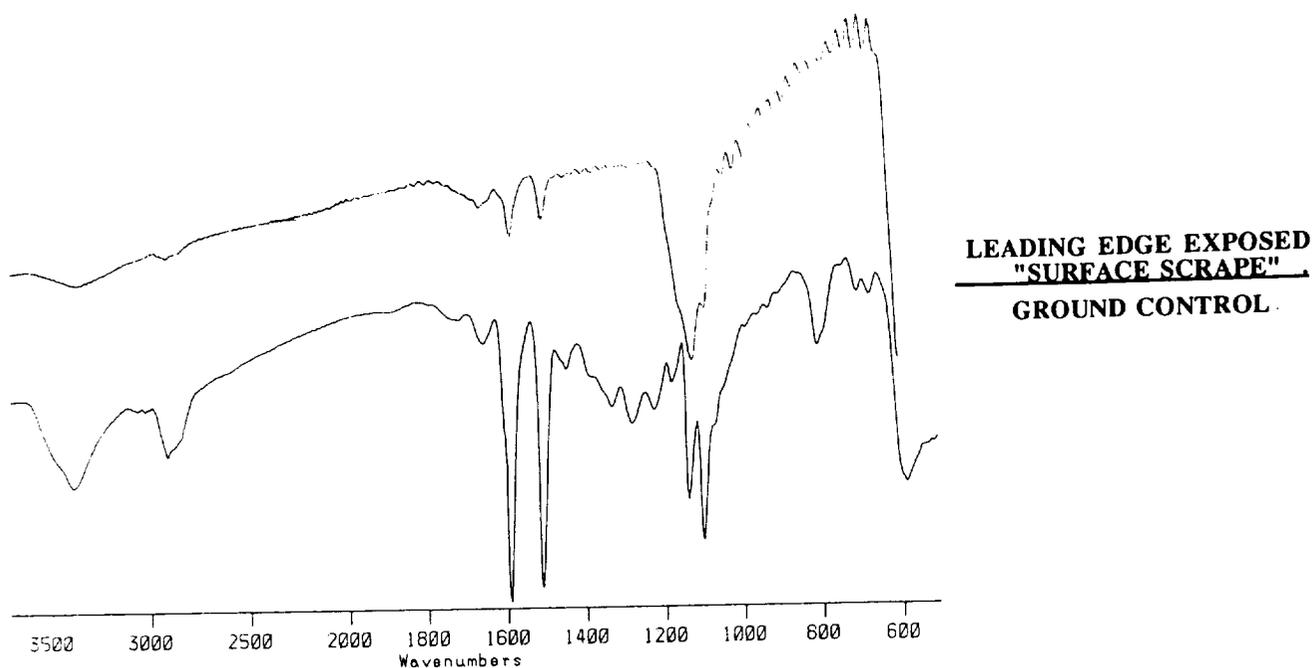


Figure 18. FTIR spectroscopy trace for 3501-6 epoxy/AS graphite specimens

The IR trace for the leading edge exposed P1700 polysulfone/T300 graphite as shown in Figure 19 also shows the presence of a broad peak in the 1100 to 1200 wave number region. Comparison to the ground control indicates that most of the matrix resin has been eroded from the surface. As mentioned previously the presence of sodium sulfate has been found on the surface of the P1700 polysulfone/T300 graphite leading edge exposed specimens using X-ray diffraction. The source of sulfur in this case may be the sulfur incorporated into the backbone of this polymer system.

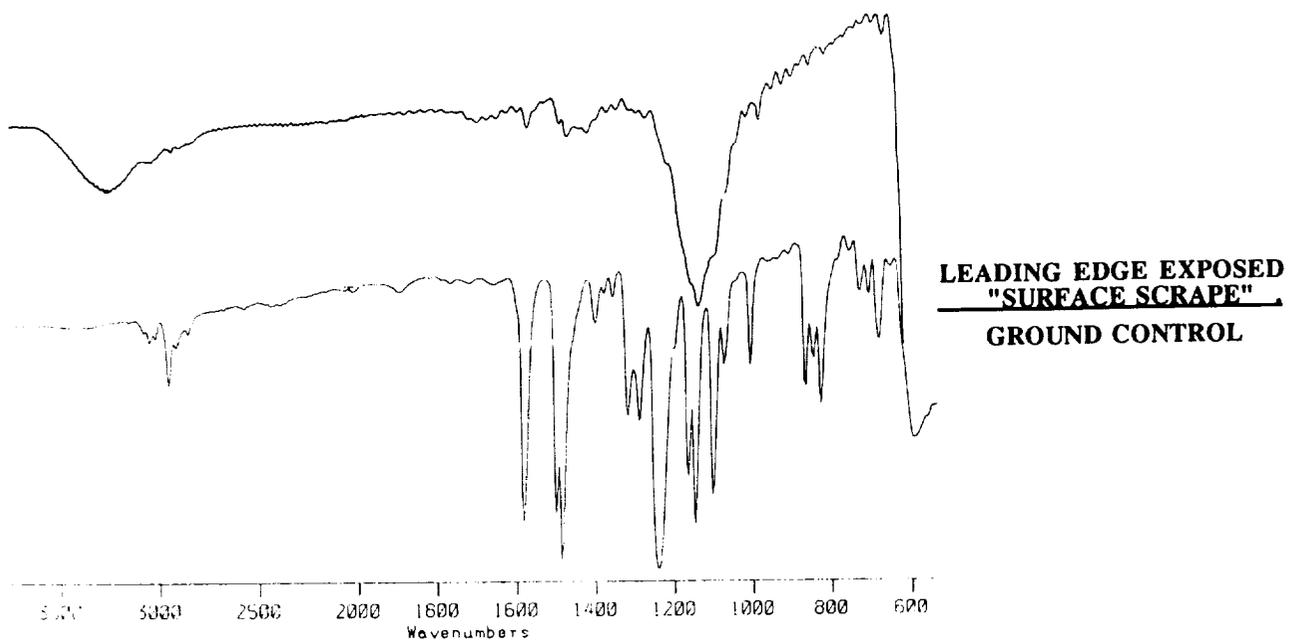


Figure 19. FTIR spectroscopy trace for P1700 polysulfone/T300 graphite specimens

Figures 20 and 21 show the IR traces for the PMR-15 polyimide/C6000 graphite and LARC160 polyimide/graphite leading edge exposed surface and ground control specimens. These spectra are very similar reflecting their similar chemistry. Unlike the epoxy and polysulfone exposed surfaces the polyimides appear to have retained more characteristic peaks for the matrix material indicating more exposed polymer remaining on the surface. The only significant differences are disappearance and/or weakening of peaks and shoulders at 1660, 1600, and 930 wave numbers from the ground control to the exposed trace. These differences were also present for the PMR-15 polyimide/C6000 graphite specimens examined from experiment M0003-8.² Changes in absorption in these bands may be attributable to changes in the carbonyl linkages between the phenyl rings.⁶ This area warrants further investigation as these changes may offer insight into the chemical breakdown mechanism of polyimides in an atomic oxygen environment.

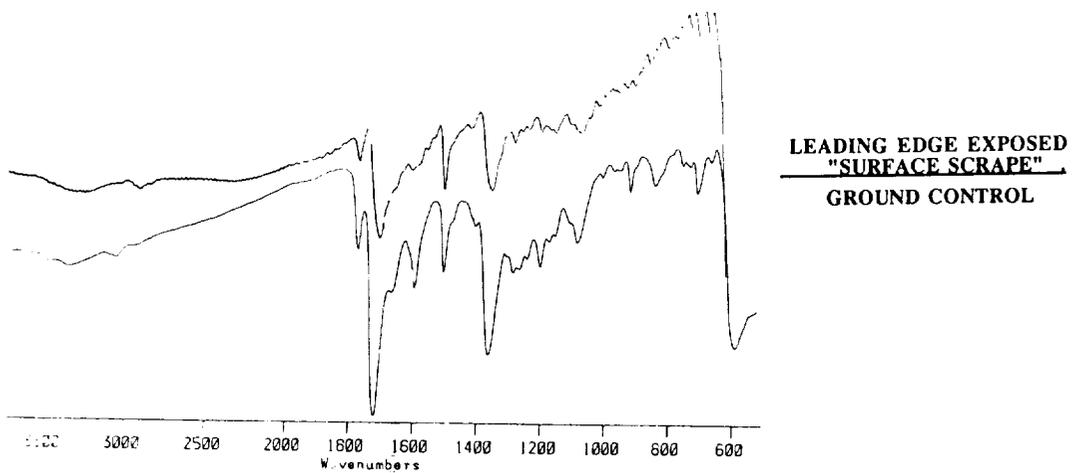


Figure 20. FTIR spectroscopy trace for PMR-15 polyimide/C6000 graphite specimens

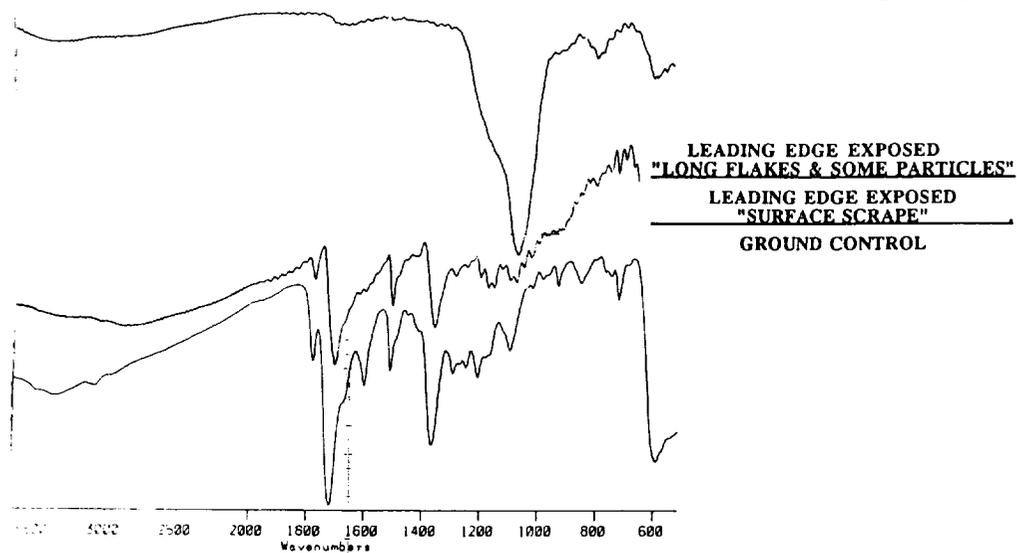


Figure 21. FTIR spectroscopy trace for LARC 160 polyimide/graphite specimens

Energy Dispersive X-ray spectroscopy was performed on shielded, exposed and ground control specimens. Also, portions of the ground control were split open to reveal fresh material. Figure 22 summarizes the results. Contamination was found on all of the surfaces making comparison of test results difficult. However some clear trends were distinguishable.

Sulfur and silicon were present to some extent on all surfaces. The epoxy and polysulfone specimens displayed a strong presence of both sulfur and sodium on the surfaces. However, the polyimides did not have sodium present and only a trace of sulfur was found. Other than the heavy background noise associated with carbon the only distinguishable material found on the freshly exposed interior surfaces of the ground controls was silicon. This presence of silicon was extremely weak.

These test results agree with the previously mentioned findings of sodium sulfate on the surfaces of the epoxy and polysulfone specimens. The silicon contamination found on most surfaces of LDEF was also present on these specimens.

- STRONG SULFUR AND SODIUM PEAKS FOR EXPOSED LEADING EDGE SURFACE "ASH" OF EPOXIES, POLYSULFONE.
- SODIUM NOT PRESENT, SULFUR VERY WEAK FOR EXPOSED LEADING EDGE SURFACE "ASH" OF POLYIMIDES.
- SULFUR, SILICON PRESENT TO SOME EXTENT ON ALL SURFACES.
- SPECIMENS SPLIT OPEN TO REVEAL "FRESH SURFACES;" ONLY TRACE OF SILICON FOUND.

FIGURE 22. EDX TEST RESULTS

Figure 23 summarizes the test results and observations for the Boeing portion of sub experiment M0003-10. The most significant finding was the impact of atomic oxygen on mechanical properties. Thickness reductions for all the leading edge exposed composites resulted in reduced mechanical strength and modulus for a given specimen. Also, for the PMR-15 specimens with non 0 degree plies directly beneath a 0 degree surface ply an additional mechanical property reduction was observed. Atomic oxygen erosion resulted in unique surface textures which varied between composite types.

A residual "ash" material was observed for all atomic oxygen eroded surfaces. The level and texture of this "ash" varied between composite types. The epoxies and polysulfones displayed significantly higher levels of "ash" than the polyimides. This corresponded to the visual appearance and optical properties of the materials. Sodium sulfate was identified as a component of this "ash" for the epoxy and polysulfone composites. Attempts to isolate and identify the polyimide "ash" were unsuccessful due to the small quantities. Silicate contamination was found on all surfaces.

The only non atomic oxygen change identified was microcracking of multi-direction reinforced composites from the leading and trailing edge exposed positions. This indicates that the exposed specimens experienced higher thermal cycling extremes and/or thermal shock.

MECHANICAL: REDUCTION IN FLEXURAL PROPERTIES DUE TO AO EROSION

- Thickness loss for all leading edge exposed specimens
- Severe reduction in performance of PMR15/C6000 due to ply orientation

CHEMICAL: RESIDUAL ASH ON AO EXPOSED SURFACES

- Epoxy, polysulfone ash contains high levels of sulfur, possibly from DDS curing agent and sulfone respectively
- Polyimides had less ash on surface and could not be identified
- Silicates found on surfaces in form of "Flakes"

PHYSICAL: MICROCRACKING ONLY "NON AO" CHANGE DETECTED

- Relative reactivities (thickness reductions) of composites hard to compare due to local fiber volume and contamination variations
- No significant changes in glass transition temperatures, outgassing or thermal expansion properties.
- Microcracking occurred in multi-direction reinforced laminates
- Level of microcracking varied with severity of temperature fluctuations

FIGURE 23. SUMMARY

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